MAY 30 '86
206
4/31-L-12
EP1.89/2:600/S4-85/078

United States Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Las Vegas NV 89114

Research and Development
EPA/600/S4-85/078 Jan. 1986

EPA

Project Summary

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GC/FT-IR and GC/FT-IR/MS Techniques for Routine Environmental Analysis

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This report documents progress on three tasks related to the design and testing of procedures and techniques for analyzing volatile and semivolatile components of environmental samples. The tasks include (1) develop and test a procedure to use infrared molar absorptivities and internal standards for the routine quantification of environmental contaminants, (2) prepare and test computer software to use for the on-the-fly analysis (both qualitative and quantitative) of mixtures of volatile components by direct-linked gas chromatography/Fourier transform infrared/mass spectrometry, and (3) develop, test, and construct a high-sensitivity gas chromatography/Fourier transform infrared system, and retrofit the Fourier transform infrared spectrometer at the Environmental Protection Agency's Environmental Monitoring Systems Laboratory in Las Vegas, Nevada.

In response to Task 1, a method to estimate the quantity of each component separated by gas chromatography based on the results of a spectral search program is described, and an approach to improve the quality of the infrared vapor-phase spectral data base is suggested.

In response to Task 2, an interface between a gas chromatograph, a Fourier transform infrared spectrometer, and a Fourier transform mass spectrometer is described. An algorithm to improve the certainty of identifying materials through both their infrared and mass spectra is discussed. A quadrupole mass spectrometer has been purchased and tested, and a gas chromatograph/Fourier transform infrared/mass spectrometer system based on this instrument is being constructed.

In response to Task 3, methods of improving the sensitivity of the interface between a gas chromatograph and a Fourier transform infrared spectrometer have been investigated. A method of decreasing the nonlinearity of the detector response introduced by unmodulated emission from the hot lightpipe through cooled apertures is described. Techniques to simultaneously increase the sensitivity of gas chromatography/Fourier transform infrared measurements and to decrease the nonlinearity of detector/amplifier response through the use of optimal optics and small focal area detectors are discussed.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Currently the U.S. Environmental Protection Agency (EPA) screens the gas chromatographicable portion of sample extracts for a few hundred target organic compounds. Since over sixty thousand manufactured chemicals are currently regulated under the Toxic Substance Control Act, it is apparent that many regulated compounds are not identified (let alone determined) in environmental samples. The present protocol for the analysis of

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volatile and semivolatile compounds by the EPA involves a separation by gas chromatography (GC) and measurement of the mass spectrum of each separated component. Mass spectrometry (MS) is a fast, sensitive, instrumental analytical technique, and the linkage of gas chromatography and mass spectrometry (GC/MS) represents a good first step towards the total characterization of environmental samples. Nevertheless, GC/MS does have several drawbacks.

First, the mass spectra of many isomeric compounds are very similar, yet the toxicity and/or carcinogenicity of the individual isomers may be very different. For certain compounds, it may be difficult to produce a discernable molecular ion when ionization is initiated by electron impact (EI), and, even when chemical ionization (CI) methods are used, the molecular ion (M+) of certain compounds may be present at a level considerably below the intensity of other ions in the mass spectrum. Under these circumstances, *a priori* interpretation of the mass spectrum may be difficult if not impossible. Finally, even a semiquantitative determination of all peaks in the gas chromatograms of complex environmental samples is usually impossible without an unambiguous identification of each peak component and the availability of calibration standards for each component.

The application of Fourier transform infrared spectrometry (FT-IR) in place of mass spectrometry, as well as the application of FT-IR in addition to mass spectrometry for the identification of components separated by gas chromatography (GC/FT-IR and GC/FT-IR/MS, respectively) has been proposed as an alternative technique to GC/MS. Although GC/FT-IR measurements may never have superior sensitivity to the corresponding GC/MS measurements, the capability of infrared spectrometry to distinguish between isomers and the reproducibility of GC/FT-IR spectra from one instrument to another should enhance the potential for unambiguous structural assignments of components of complex mixtures separated by GC. Because of the greater reproducibility of infrared spectra, relative to GC/MS spectra (reproducibility requires precise quadrupole tuning), GC/ FT-IR also has the potential to improve the capability of obtaining estimates of the quantity of each component eluting from the chromatographic column, whether or not this molecule has been unequivocally identified or has merely been assigned to a certain chemical class.

Results and Discussion

Quantitation Without Identification (Task No. 1)

This task involves the development of a technique for obtaining an estimate of the quantity of each GC eluate from its GC/FT-IR spectrum. An initial approach based on the assumption of a constant molar absorptivity was eventually abandoned in favor of a technique that appears to have the potential of giving a far superior result. Through an internal search of EPALIB, it was recognized that the best matches to the spectrum of a selected probe molecule often had similar structures. The molar absorptivities of these compounds also were often found to be quite similar. For a given peak in the chromatogram, a good match will be obtained if the reference spectrum of that compound is in the data base. In this case, the amount of sample passing through the lightpipe can be estimated from the quantitative information given in the EPALIB header and the lightpipe dimensions and carrier-gas flow rate.

If the "unknown" is not represented in the data base, a spectral search will lead to the closest analogs to the correct molecule appearing in the search output. In fact, even if a reference spectrum of this sample *is* in the data base, it can often be difficult to unequivocally assign its chemical structure because of the effect of spectral baseline noise, coelution peaks, or the presence in the data base of reference spectra of compounds with a similar chemical structure. We have, therefore, developed a method for estimating sample quantity based on the hit quality index (HQI) of a spectral search. The quantitative information listed in the header of each reference spectrum in EPALIB is weighted by the reciprocal of the HQI to derive a quantitative estimate of the amount of sample present in the lightpipe. The HQI is a measure of the difference between the spectrum of the unknown and of each reference spectrum in the data base. The procedure we are developing takes the quantitative value afforded by each of the top search hits and weights them by the reciprocal of the HQI.

For some compounds, the results of this approach were excellent. For example, the value of sample quantity calculated for phenol from the five closest matches was only in error by 3 percent from the value listed in the EPALIB header for phenol. Other compounds, especially those with exceptionally high peak absorptivities, gave poorer results. Nevertheless, for the great majority of compounds tested, the error was less than a factor of two. In the second year of this project, further investigations of this technique will be made. This approach is most promising for the nontarget compound analytical situation in which the unknown analyte's spectrum is rarely in the search library.

The GC/FT-IR/MS Interface (Task No. 2)

A linked analytical technique comprising capillary GC/FT-IR/MS can provide chemical information about mixtures of volatile and semivolatile compounds to aid in component elucidation. The infrared and mass spectral data generated are complementary and can be combined to give a less ambiguous chemical identification. In the initial phase of this work a Fourier transform mass spectrometer (FT-MS) was used to measure the mass spectra. At the end of the first year a quadrupole mass spectrometer (Hewlett-Packard Mass Selective Detector) was installed.

There are several advantages to using an FT/MS in this system. Besides the high-split ratio, which allows almost all of the GC effluent to pass to the less sensitive FT-IR, several types of mass spectral data can be obtained during one chromatographic run. Due in part to the rapid data acquisition of the FT-MS, electron impact (EI) and chemical ionization (CI) mass spectra can be acquired alternately. To prevent CI reagent gas (methane) from interfering in EI acquisition, the gas is pulsed into the FT-MS only during the CI experiment. To demonstrate that the interface is amenable to the study of complex mixtures, a peppermint oil was analyzed. This sample contains potentially difficult compounds to identify. This oil, however, has been characterized by a chromatographic supplier and can be considered as a "known" sample. Peppermint oil contains isomers of cyclic hydrocarbons as well as isomers of cyclic ketones. The concentration dynamic range was also a concern, because 95 percent of the sample is represented by only a few components.

The spectral library search results from the GC/FT-IR/MS experiment are very informative in themselves (Table 1). With both sets of data, a very powerful identification tool is possible. One may ask, however, whether one set of results should be weighted against the other. An algorithm to accept or reject search-result

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Table 1. *FT-IR Library Search Results for First Peak of Peppermint Oil Sample*

EPALIB[a] Number	HQI	Identification	CAS[b] Number
2244	1318	Bicyclo/3.1.1/Hept-2-ene, 2,6,6-($C_{10}H_{16}$)[c]	80-56-8
3303	1319	Alpha Pinene ($C_{10}H_{16}$)	80-56-8
2433	1338	Pinene, 2/10/-, ($C_{10}H_{16}$)	18172-67-3
3013	1339	Bicyclo/3.1.1/Hept-2-ene-2-ethano ($C_{11}H_{1801}$)	128-50-7
2925	1352	Ethane (C_2H_6)	74-84-0
3304[a]	1353	Beta-Pinene ($C_{10}H_{16}$)	127-91-3
327	1355	Cyclohexane, 1,4-Dimethyl-, (C_8H_{16})	589-90-2
3305	1356	Beta-Pinene ($C_{10}H_{16}$)	127-91-3
121	1360	Cyclohexane, Cis-1,3-Dimethyl-, (C_8H_{16})	638-04-0
457	1363	2-Butene, 2,3-Dimethyl-, (C_6H_{12})	563-79-1

[a]*Entries with an EPALIB number greater than 3300 have been added to the data base at the University of California, Riverside. The similarity of the HQI values given by the first two hits (both α-pinene but measured at different locations) is noteworthy.*
[b]*Chemical Abstracts Service.*
[c]*Elemental composition.*

combinations has recently been published. The algorithm utilizes accurate mass measurement (AMM) FT-MS results to establish the most accurate molecular formula possible. The mass error for such a determination was typically less than 10 ppm at mass 250. An error of less than 10 ppm has been found to lead to unambiguous determinations of molecular formula.

Forty-five model compounds of various group-types and polarities were used at concentrations that might typically be found in a thick-film capillary GC separation. Infrared and mass spectral search results were incorporated so that if the calculated molecular formula is not represented by any of the first five MS search results, the FT-MS search results are not used. If none of the first five matches of the IR search results coincide with the determined molecular formula, then the compound is considered unidentified. No compounds were incorrectly identified, such that the MS sampling conditions appear to be adequate. Table 2 summarizes the performance of the various algorithm combinations possible with the data collected. The accurate mass FT-IR/MS variation shows no incorrect identification and more correct identifications than FT-IR/MS without accurate mass data.

Part I: Single-Beam Studies

We have taken two approaches towards optimizing single-beam GC/FT-IR measurements. In the first, ways of modifying a standard commercial GC/FT-IR system have been investigated, while in the second, a completely new GC/FT-IR system is being designed and built.

Optimizing the GC/FT-IR Interface (Task No. 3)

Standard System Modifications

Methods are needed to reduce the signal loss that takes place at the detector when the lightpipe is heated. This decrease in signal leads to an increase in the baseline noise level in the ratio-recorded spectra and a consequent reduction in signal-to-noise (SNR). Gurka, Laska, and Titus (*J. Chromatogr. Sci.* 1982, 20:145) have shown that this effect, for temperatures ranging from ambient to 250°C, leads to a threefold loss in sensitivity. A similar profile was observed in our laboratory for measurement using a Nicolet 60-SX GC-FT-IR spectrometer. The best explanation of this effect is that the detector (and/or preamplifier) become saturated and are driven into a nonlinear response by the unmodulated infrared radiation emitted by the hot lightpipe. This heat is focused on the detector along with the modulated mid-IR radiation, causing the response of the detector to the modulated signal (the interferogram) to decrease.

We found that if a short length of lightpipe, the internal diameter (i.d.) of which was slightly bigger than the i.d. of the lightpipe, was located after the exit aperture of the lightpipe (detector end), an immediate increase in interferogram signal resulted for the Nicolet 60-SX GC/FT-IR system. The use of such an aperture, even cooled by water, made no difference at all for the older 7199 system. We also noted that when a water-cooled cone was placed over the end of the short lightpipe, a signal increase resulted even at ambient temperature. The increase in signal appears to result from a combination of the lightpipe acting as a cold shield, thus preventing unmodulated radiation from the end of the GC/FT-IR lightpipe from reaching the detector, and the cone collecting modulated radiation transmitted by the GC/FT-IR lightpipe but scattered by the heat-shield lightpipe, then passing it to the detector.

Polished aluminum cones were then fabricated to determine an optimum cone angle. The reflective cones were collecting the component of the modulated infrared signal that had been scattered by the lightpipes. A 20-percent increase in ambient signal was achieved for the 60-SX GC/FT-IR interface and as much as 38 percent increase was observed for the 7199 system with a lightpipe of same i.d. (1 mm) and similar length. We noted that positioning the cone near the lightpipe still resulted in a signal loss upon heating. A short lightpipe extension was used to move the cone further from the end of the hot lightpipe.

Design of a New Single-Beam GC/FT-IR System

To determine the optimum for GC/FT-IR lightpipes, we found it necessary to design and build an interface capable of supporting lightpipes of various dimensions while keeping set-up time to a minimum. An investigation of the optimum optical configuration for collecting

Table 2. *Comparison of Various AMM Algorithms for the 45 "Unknown" Compounds*

Algorithm	Number Identified: Correct	Incorrect	Eliminated
FT-IR	32	13	0
FT-IR/AMM	33	8	4
FT-MS	26	19	0
FT-MS/AMM	30	12	3
FT-IR/MS	32	0	13
AMM, FT-IR/MS	35	0	10

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the beam emerging from the lightpipe is being made, using lightpipes held in this variable-length oven. The goal of this study is to determine the combination of optics and detector that will result in the highest possible interferogram SNR being measured for a given lightpipe. In the experiment we are performing, a KBr lens and a detector are mounted upon a track. A lens follows the equation:

$$1/f = 1/x + 1/y \quad (1)$$

where f is the focal length of the lens and x and y are distances of the object

$$d_i = d_o y/x \quad (2)$$

where d_i is the diameter of the image at the detector and d_o is the diameter of the object (in this case, the internal diameter of the lightpipe). By varying the position of the lens and detector along the track, the tradeoffs between the solid angle of radiation collected versus detector size [and hence its noise-equivalent-power (NEP)] may be determined. The results of this experiment are very much dependent upon the lightpipe employed but should be completed in about 2 months time (September 1985). Shortly thereafter, the EMSL-LV GC/FT-IR system will be retrofitted to realize the increased sensitivity resulting from this optimized single-beam system.

Dual-Beam GC/FT-IR

The complete design of a dual-beam system is necessarily dependent upon the results of the investigation into single-beam GC/FT-IR systems. For this reason, much of the design is yet to be completed. One area in which we have been involved during the first year of this project is the construction and evaluation of a dual-element detector. By utilizing a detector with dual elements housed within the same dewar, we believe that nonlinear conditions (observed at high levels of radiation flux incident upon the large single detector used in a dual-beam FT-IR system) may be avoided by dividing the energy between two elements rather than concentrating it on one. These elements must be closely matched to optimize the signal-addition step, which is carried out electronically before the resultant interferogram is digitized.

Conclusions and Recommendations

Task 1

a. Measurements of the absorbance of the most intense peak in the spectrum or that of certain functional groups does not permit the quantity of a given component present in the lightpipe to be determined accurately.

b. A method based on a weighted average of the quantities of the samples given as the top few matches by spectral searching routines appears to have great potential for allowing the quantity of an unidentified peak component to be estimated.

c. A major limitation to this method appears to be the quantitative accuracy of the EPA library of vapor-phase infrared spectra (EPALIB).

d. We recommend that efforts to improve the quality and size of GC/FT-IR reference data bases be renewed, possibly through the initiation of a collection of reference spectra submitted to a central computer by current GC/FT-IR users. This is an economic approach to increasing the data base because reference spectra would be donated.

Task 2

a. A parallel interface between a gas chromatograph, an FT-IR spectrometer, and a Fourier transform mass spectrometer was constructed and was applied to the identification of the components of several complex mixtures.

b. Accurate mass measurements have been used to establish the molecular formula of GC eluates and when combined with infrared spectral search data, accurate mass measurements appear to present a powerful method for compound identification.

c. A low-cost quadrupole mass spectrometer has been installed and will be interfaced first to a commercial GC/FT-IR interface and then to an optimized GC/FT-IR interface being constructed under Task 3.

Task 3

a. Methods of reducing the effect of detector nonlinearity because of unmodulated radiation emitted by the lightpipe are being developed.

b. The use of a cooled lightpipe in conjunction with a cone to collect scattered radiation has been shown to improve the sensitivity of a commercial GC/FT-IR system.

c. An optical configuration has been designed to reduce the size of the infrared detector below the size of detectors now being used in commercial GC/FT-IR systems. This will result in an increased system sensitivity.

In conclusion, prospects are high for the construction of a directly linked GC/FT-IR/MS system in which the FT-IR sensitivity is over an order of magnitude more sensitive than are currently marketed FT-IR systems. Computer software is being prepared to aid in evaluating the large quantities of analytical data that will be generated by such a system. Techniques are being developed in an attempt to semiquantitate by FT-IR without complete analyte identification, and to quantitate FT-IR identified compounds without quantitation calibration curves by means of infrared absorption coefficients. These quantitation techniques cannot be achieved by conventional GC/MS and should result in reduced analytical costs because of reduced spectrometer data acquisition time. The optimized GC/FT-IR/MS system should provide a much larger amount of analytical information than that obtainable from GC/MS used alone.

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The complete report, entitled "GC/FT-IR and GC/FT-IR/MS Techniques for Routine Environmental Analysis," (Order No. PB 86-128 584; Cost: $9.95, subject to change) will be available only from:

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